

Abstract: Study of the dynamics of oxygen adsorption on Ir(111)*

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Under ultra-high-vacuum conditions, the chemisorption of oxygen on Ir(111) has been found to proceed via a mobile precursor state. This state appears to be physically adsorbed oxygen molecules acting as a two-dimensional gas. Auger spectroscopy, contact potential difference measurements and thermal-desorption mass spectrometry suggest that the sticking probability into the chemisorbed state is constant until saturation coverage is very nearly reached. The sticking probability at 325 K is 0.09, but it *increases* continuously with decreasing temperature until a value of 0.18 is found at 225 K (the lowest temperature investigated). The accuracy of this observed trend is considerably greater than the accuracy associated with each individual measurement of which the latter is on the order of 50%.

A temperature-dependent temporal delay was noted with LEED for the formation of three independent, ordered domains of (2×1) superstructure, each rotated 120° with respect to one another. Although the apparent dimensionality of the LEED superstructure was (2×2) , the corresponding absolute coverage was measured by x-ray photoelectron spectroscopy (XPS) to be 7.8×10^{14} O atoms/cm². This is indicative of half-monolayer surface coverage at saturation, which is consistent with the (2×1) domain structure. The measured delay, or induction periods (as a function of surface temperature) indicate that the activation energy for surface diffusion leading to the ordering is between 16 and 19 kcal/mole. The LEED also shows that the chemisorbed oxygen atoms undergo an order-disorder transition on the surface with an energy difference between the ordered and disordered states of approximately 1 kcal/mole. The data are consistent with a two-dimensional Ising model with a critical

temperature for disorder of approximately 460 K.

Mass spectrometry results show that the heat of adsorption of the chemisorbed atomic oxygen is $(65 - 10\theta)$ kcal/mole where θ is the fraction of saturation coverage (not absolute fractional coverage). The oxygen desorbs according to second-order kinetics verifying that the chemisorbed state is dissociated oxygen.

At $T \geq 700$ K, the chemisorbed oxygen is incorporated into the Ir forming a chemically inert nonstoichiometric near-surface oxide state. In particular, this oxide state is not reactive toward either CO or H₂ in a temperature regime where the chemisorbed oxygen overlayer reacts rapidly. The oxide state decomposes, with the evolution of molecular oxygen, at approximately 1270 K with a kinetic order of unity. The conversion of the oxygen overlayer into the near-surface oxide may be observed directly by means of XPS measurements. There is a chemical shift in the binding energy of the O(1s) level of the chemisorbed oxygen overlayer (529.8 eV) and the near-surface oxide (531.5 eV). Further details concerning the interaction of oxygen with the (111) surface of Ir may be found in Refs. 1-3.

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³ S. P. Withrow and W. H. Weinberg (to be published).